HYDROLOGICAL PROCESSES
Hydrol. Process. **15**, 1347–1362 (2001)
DOI: 10.1002/hyp.215

Applicability of NASQAN data for ecosystem assessments on the Missouri River

Dale Blevins[1]* and James Fairchild[2]
[1] *US Geological Survey, Water Resources Division, Room 221, 301 W. Lexington, Independence, MO 64050, USA*
[2] *US Geological Survey, Biological Resources Division, 4200 New Haven Road, Columbia, MO 65201, USA*

Abstract:

The effectiveness of ecological restoration efforts on large developed rivers is often unknown because comprehensive ecological monitoring programs are often absent. Although Eulerian water-quality monitoring programs, such as the National Stream Quality Accounting Network (NASQAN) program, are more common, they are usually not designed for ecological assessment. Therefore, this paper addresses the value of NASQAN for ecological assessments on the Missouri River and identifies potential program additions and modifications to assess certain ecological changes in physical habitat, biological structure and function, and ecotoxicity.

Five additional sites; the analysis of chlorophyll, mercury, ATP, potential endocrine disruptors, total trace elements, and selected total hydrophobic organics; and the hourly measurement of dissolved oxygen, turbidity, and temperature are recommended. Hourly measurements would require an entirely new operational aspect to NASQAN. However, the presence of data loggers and satellite transmitters in the gauging stations at all NASQAN sites substantially improves the feasibility of continuous water-quality monitoring. The use of semipermeable membrane devices (SPMDs) to monitor dissolved bioaccumulating organics and trace elements, identification and enumeration of zooplankton, and characterization of the bioavailability of organic matter are also recommended.

The effect of biological processes on the conservative assumptions that are used in flux and source determinations of NASQAN constituents are also evaluated. Organic carbon, organic nitrogen, dissolved phosphate, and dissolved inorganic nitrogen are the NASQAN constituents most vulnerable to biological processes and thus violation of conservative assumptions.

KEY WORDS Missouri River; NASQAN; water-quality networks; ecological monitoring; water quality; aquatic ecology; large rivers; ecotoxicity

BACKGROUND AND OBJECTIVES

Most large rivers in developed countries have been highly modified by dams, channelization, and bank stabilization. Changes in management of large developed rivers to enhance ecological functions have often been proposed. However, the effectiveness of proposed changes usually cannot be determined because ecological monitoring programs are largely absent. Water-quality monitoring programs, such as the US Geological Survey's National Stream Quality Accounting Network (NASQAN) program, are more common, although they are not usually designed to assess ecological questions. The primary purposes of this paper are, therefore, to evaluate the uses of NASQAN data for ecological assessment and to identify additions or modifications that could improve NASQAN's capacity for ecological assessment, while capitalizing on the existing water-sampling infrastructure. Ecologic assessment in this paper refers to the determination of changes in the character and extent of ecologic functions of large rivers in response to anthropogenic activities. Such assessments are needed to maximize the ecological benefits of restoration efforts and minimize adverse effects on other river uses. Ecological assessments include the measurement of ecological response and

* Correspondence to: D. Blevins, US Geological Survey, Water Resources Division, Room 221, 301 W. Lexington, Independence, MO 64050, USA. E-mail: dblevins@usgs.gov

Received 1 December 1999
Accepted 15 May 2000

indicator variables such as species populations, diversity, and sustainability, as well as understanding the interactions of physical, chemical, and biological elements of a river. The primary use of Eulerian networks, such as NASQAN, is often to determine constituent fluxes and source areas, and conservative behaviour of constituents while in transit is assumed. However, biological processes can transform or even remove some constituents, thus violating conservative assumptions. The susceptibility of sampled constituents to nonconservative biological processes needs to be assessed. Given this context, the following questions are addressed in this paper.

(1) What do Eulerian hydrochemical monitoring programs, such as NASQAN, tell us about ecosystem processes in large rivers?
(2) What modifications are needed to address ecological questions?
(3) What effects do ecological processes have on NASQAN constituents and subsequent interpretations about their source, transport, seasonal patterns, speciation, and phase?

The Missouri River was chosen as a case study because it has many issues and characteristics in common with many other large rivers in developed countries. These characteristics include impoundment, flow regulation, channelization, dredging, dyking, and drainage of associated wetlands (Funk and Robinson, 1974). These developments serve many interests, including agriculture, shipping, industry, and recreational

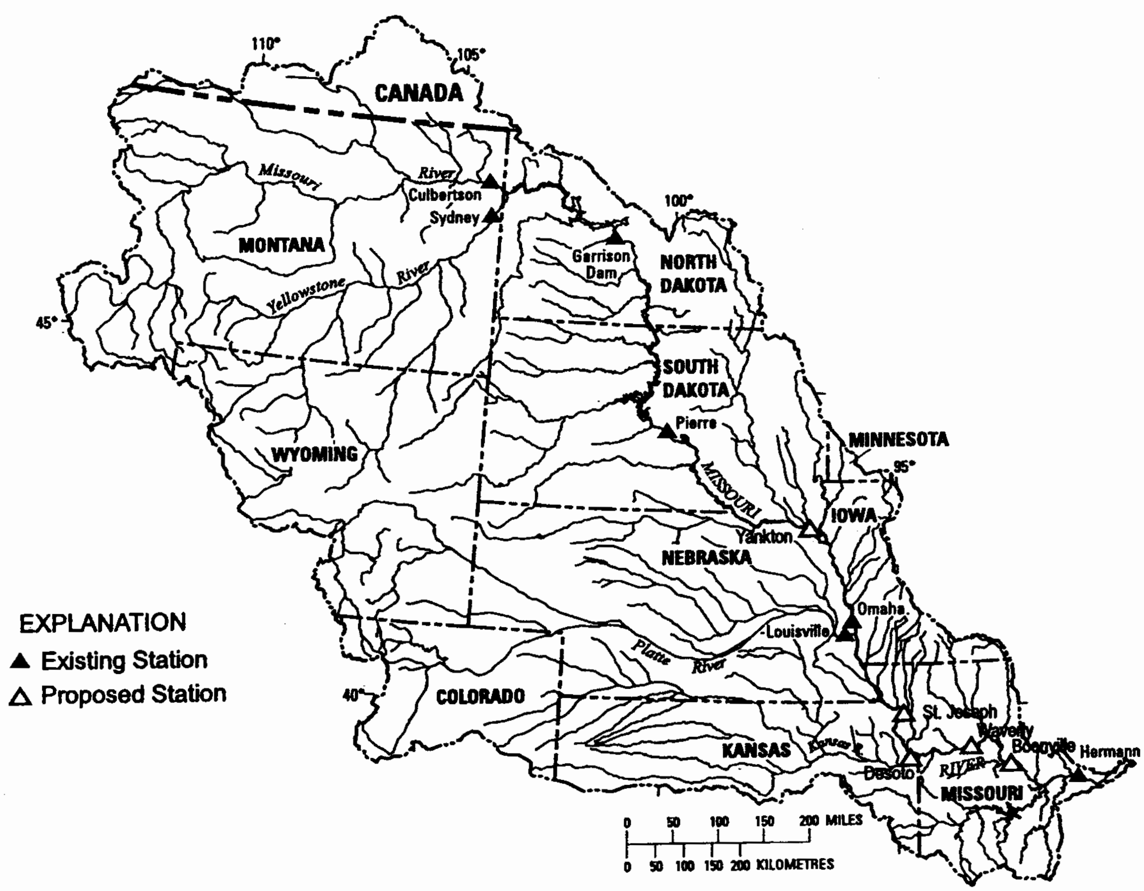

Figure 1. Location of NASQAN stations in the Missouri River Basin

Published in 2001 by John Wiley & Sons, Ltd. *Hydrol. Process.* **15**, 1347–1362 (2001)

Table I. Selected characteristics of NASQAN sampling sites in the Missouri River Basin

USGS station number	Latitude	Station name	Distance (km) above mouth	Drainage area (km^2)	Mean discharge (m^3s^{-1})	Event samples per year	Total samples per year
06934500	39°42′36″	Missouri River at Hermann, MO	158	1 550 000	186	3	15
06610000	41°15′32″	Missouri River at Omaha, NE	992	1 340 000	68·2	3	15
06805500	41°00′55″	Platte River at Louisville, NE	26·6	222 200	14·4	3	15
06440000	44°22′33″	Missouri River at Pierre, SD	1716	630 700	60·6	0	6
06338490	47°30′08″	Missouri River below Garrison Dam, ND	2236	469 800	46·8	0	6
06185500	48°07′30″	Missouri River near Culbertson, MT	2610	237 200	22·2	3	9
06329500	47°40′42″	Yellowstone River near Sidney, MT	46·7	179 000	26·9	3	12

interests (Hesse *et al.*, 1989). Most recently, interest in restoration of ecological functions of intensely managed rivers such as the Missouri has become widespread. However, resolving conflicts to meet multiple uses and benefits requires information necessary to understand the complex physical, chemical, and biological relations in large rivers. The lack of data needed to assess ecological accommodations to the Missouri River has been recognized by many river scientists and managers (Missouri River Natural Resources Committee, 1998). Ecological conditions and responses to river management changes must be monitored and quantified to maximize ecological benefits while minimizing adverse effects on other uses.

NASQAN is used in this paper for comparisons and a base for an aquatic ecosystem monitoring program for the Missouri River. Seven NASQAN sites in the Missouri River basin (Figure 1) are currently sampled for about 100 dissolved constituents and 30 suspended constituents (Hooper *et al.*, 2001) including eight major ions, 47 major pesticides, 22 trace elements, ten nutrients, and several other physical and support measurements. The seven sites are sampled either 6, 9, 12, or 15 times per year, as described in Table I. Sample frequency varies depending on the characteristics of each station. For example, stations in the free-flowing reaches (e.g. Missouri River at Hermann and Omaha, and Yellowstone and Platte Rivers) are sampled approximately monthly in addition to three annual high-flow samples, whereas sites just below dams (Missouri River at Culbertson, below Garrison Dam, and at Pierre) are sampled only six times per year because of moderation of discharge and chemical variability by the reservoirs.

WATER-QUALITY MEASURES OF ECOSYSTEM CHARACTER ON THE MISSOURI RIVER

NASQAN is the primary water-quality monitoring program on large rivers in the USA and is designed to determine fluxes and sources of constituents that can affect human health, water use, and recreation (Hooper *et al.*, 2001). NASQAN and other national networks usually contain fixed-station, fixed-time interval

(Eulerian) elements. However, ecological processes are highly variable in time and space, and flux and source determinations are only a subset of those needed for comprehensive ecological assessments. Therefore, the site selection, sampling frequency, and constituents used in hydrochemical monitoring are not necessarily optimal for ecological assessment. Even with adjustments, Eulerian water-quality networks cannot be expected to address some ecological issues, even at a basin scale. Although a certain amount of ecological information can be derived from existing data, the adequacy of existing water-quality monitoring programs to assess ecological functions needs to be examined.

In order to design a water-quality network for ecological monitoring, important water-quality measures of critical ecological processes must be identified. Not all ecological measures are suitable for Eulerian networks, because fixed-station networks on large rivers are limited to parameters that can be measured at points or river transects. Parameters that have large longitudinal variabilities are typically not suited for fixed-station sampling. The range of variability of these parameters must be evaluated in order to determine the appropriate sampling frequency and location for these measurements. Any adjustments to a water-quality monitoring program to accommodate ecological assessments depend on the specific objectives of the assessment. Therefore, in this section, critical water-quality measures will be identified based on known ecological characteristics of the Missouri River. The recommended frequency and spatial separation of measurements will be based on expected temporal variability, downstream changes in ecological character, and on the objective of assessing changes in ecological function caused by changes in flow management and ecological restorations. These monitoring characteristics will then be compared with current national networks.

Water quality is an important measure of ecosystem function because it can either control functions or change as a result of these functions. Most riverine-ecosystem characteristics affected or indicated by water quality can be put into three categories: physical habitat characteristics; biological structure and functions; and ecotoxicological characteristics. Some constituents and properties affect more than one category, but these classifications are useful for organizing and determining water-quality measurements needed for ecosystem characterization.

Measures of habitat amenable to Eulerian water-quality networks

The physical and chemical habitat of the Missouri River has been altered dramatically by anthropogenic activities such as construction of main stem dams, channelization, and bank stabilization activities; this has altered hydroperiods, temperature, depth, velocity, turbidity, sinuosity, bed materials, and chemistry in many areas of the river. Each of these factors is critical to aquatic habitat. Although Eulerian water-quality networks cannot be expected to characterize all these attributes, fixed-station sampling can provide important information about some habitat characteristics. Habitat is defined here as the sum of the conditions where river organisms live and is primarily used to categorize ecological measurements.

Hydrologic measures. Hydrologic processes, such as dilutions and loadings from tributaries, can be a larger factor than biologic processes in determining concentrations of many suspended constituents, especially in the winter when most biologic processes stop (Leenheer *et al.*, 1995). Biological communities have evolved in large rivers in relation to seasonal patterns in discharge that control reproductive cues such as temperature, light, current velocity, and perhaps biochemical factors. Historically, flow in the Missouri River exhibited a distinct spring/summer rise that resulted in overbank flood events (Galat *et al.*, 1998). These early summer floods imported allochthonous (material derived from outside the river) organic matter and nutrients into the river, while also providing warmer thermal regimes and better bioenergetic conditions for fish and invertebrates. However, impoundment and channelization have caused significant alterations in the hydroperiod and availability of flood-plain habitat. These changes have been implicated in declines in populations of many large river benthic fishes (Galat *et al.*, 1998). Recent flood-plain restoration efforts that have removed levees are suspected of decreasing the stage of floods in some areas. For these reasons, the spacing of both streamflow and sampling stations is important and should largely be based on the location of large tributaries and potential flood-plain habitat. Discharge and stage are measured continuously at all NASQAN sites and at 13 other sites on the Missouri River, and stage alone is measured continuously or daily at several other sites. With this spatial and temporal definition, contributions from all major tributaries are captured and interpolations of discharge based on stage, distance, or drainage area are reasonably accurate. At ungauged sites where precise stage information is needed, spot measurements of stage can be made and regressed against stage at nearby gauges to estimate stage during unmeasured times. Consequently, existing stage and discharge monitoring probably are adequate for most ecological studies.

Separation of NASQAN sites by latitude, distance, and discharge are shown in Table I. The largest changes in distance, discharge, latitude, and human population occur in the reaches between Omaha and Hermann and between Pierre and Omaha. Addition of sites in these two reaches would substantially improve the ability of NASQAN both to identify sources of chemical constituents and characterize longitudinal changes on habitat variables. An additional site at Yankton, SD, would substantially decrease the distance and latitude gaps between Pierre and Omaha. The Yankton site would need less frequent sampling because of its location immediately below the most downstream reservoir, but it would describe a critical change in ecological processes from lentic to lotic conditions (i.e. serial discontinuity) (Ward and Stanford, 1983). Temperature, dissolved oxygen, and turbidity would be expected to change rapidly in this reach. Potential additional sites between Omaha and Hermann at St Joseph, Waverly, and Boonville (all in Missouri) would decrease latitude changes and the incremental changes in discharge between sites to about 20%. These sites, with another site at the mouth of the Kansas River, a major tributary, would also isolate the effects of the Kansas City metropolitan area, the largest urban development in the basin.

Sediment and turbidity. Historically, the Missouri River was strikingly turbid even when first described by Father Jacques Marquette in 1673:

> '... we heard the noise of a rapid, into which we were about to run. I have seen nothing more dreadful. An accumulation of large and entire trees, branches, and floating islands, was issuing from the mouth of the river Pekitanoui (Missouri River), with such impetuosity that we could not without great danger risk passing through it. So great was its agitation that the water was so very muddy, and could not become clear' (Margry, cited in Mathews (1961)).

Large rivers generally have high abiotic turbidities that control light penetration, and thus, primary productivity (Horne and Goldman, 1994). Turbidity also affects the top of the food web, as it can limit the survival of predatory, sight-feeding fish. Low visibility streams often are dominated by fish that do not rely solely on sight to find food (e.g. sturgeon (family Acipenseridae), catfish (*Ictalurus*), and buffalo (*Ictiobus*)). However, main stem dams and channel stabilization have substantially decreased turbidity, which may disadvantage tactile species such as the endangered pallid sturgeon (*Scaphirhynchus albus*). Decreases in turbidity also may have allowed increases in primary production in reaches just below the lowest reservoir (Ward and Stanford, 1983). Therefore, turbidity is a basic and important ecological measurement with controlling impacts at opposite ends of a food web.

Although turbidity measurements are made on all NASQAN samples, six to 15 measurements per year are not adequate to track the rapid variability that often occurs with flow. Consequently, peak and minimum turbidities are missed, and seasonal patterns and long-term trends are difficult to detect and quantify without many years of data. Therefore, it would be optimal to measure turbidity at either daily or hourly intervals.

Suspended-sediment concentration is an important factor controlling turbidity and, thus, has a great effect on the ecological structure of the river. The particle size and organic content of the sediment also have substantial impacts on a food web based largely on detritus. Therefore, suspended sediment is an important measure of ecological character. Suspended sediment is analysed at all NASQAN sites, although the variability of sediment concentrations is not well characterized by 15 samples a year. However, because suspended sediment varies with discharge, turbidity, and other variables, multiple regressions can be used to estimate daily suspended-sediment concentrations, if continuous turbidity monitoring is added. A substantial reduction of estimation error may also be achieved through use of Kalmon smoothing techniques (Holtschlag, 2001) and adding samples collected at times of unusually high or low suspended-sediment concentration.

The size of particulates in NASQAN samples is partially characterized by determinations of sand content (particles with diameters greater than 0·062 m). The sand fraction, which often is half of the suspended sediment on the lower Missouri River (downstream of Gavins Point Dam, South Dakota) (US Geological Survey, 1973–1998), is mostly inorganic and, therefore, largely inert. Although further particle-size analyses would be useful for some detailed studies, sand–silt breaks are adequate for identifying the biologically active portion. Colloid content is not broken out in NASQAN samples, but three samples collected near the mouth of the Missouri River by Rostad and Leenheer (1997) in 1991 and 1992 had colloid concentrations that ranged from 3 · 1 to 5 · 6% of the total particulate concentration, which is substantially less than the Mississippi and Ohio Rivers. This small sample indicates that determination of colloidal concentrations may not be a critical factor in physical characterization of suspended sediment.

Temperature, dissolved oxygen, and specific conductance. Water temperature is one of the most important factors controlling rates of aquatic biological activity (Horne and Goldman, 1994) and is, therefore, a critical biological measurement. Water temperature is measured when NASQAN samples are collected, but six to 15 measurements per year do not characterize periods of biological activity with much precision. Also, given the large range in latitude covered by the Missouri River, upstream and downstream changes in temperature are not adequately defined by the seven NASQAN sites scattered over the river's 3768 km length. Although weekly temperature measurements would likely suffice for many time-trend and ecological assessments, both spatial and temporal variation of water temperature could be defined with hourly temperature measurements with little difficulty at all 18 stream-gauging stations on the river.

Dissolved oxygen is measured at all NASQAN sites with all samples and is both an ecological driver and an ecological indicator that fluctuates daily and hourly. Consequently, six to 15 measurements per year do not capture maximum and minimum dissolved-oxygen events. Dissolved oxygen in the lower Missouri River is affected strongly by season and the input of oxygen-demanding substances. During summer stage rises, concentrations of dissolved oxygen often measure less than 5 mg L^{-1} and have been measured as low as 1 mg l^{-1} (US Geological Survey, 1973–1998). These sags, noted as early as 1913 (Ford, 1982), can last from a few days to a few weeks and can affect some aquatic species. The dissolved oxygen content of reservoir outflows can also be low if withdrawals are made from the hypolimnion or they are supersaturated by the turbulence of releases and affect aquatic species immediately downstream. Therefore, dissolved oxygen is an important ecological measurement that needs to be measured hourly or daily in the summer to capture the variability and characterize periods and reaches of low concentrations. The lack of low dissolved-oxygen concentrations measured in the upper river indicates that the current spacing of water-quality stations is adequate, though additional stations at Yankton, SD, and Waverly, MO, could help determine the spatial extent of low dissolved-oxygen events in the lower river.

Specific conductance is an indicator of the dissolved ionic content of water and is measured in all NASQAN samples. Generally, specific conductance increases in the reservoirs, peaking below the most downstream dam and then decreases downstream to the mouth (Figure 2) (Kelly and Hooper, 2001). Although specific conductance is diluted by rainfall, the historic range of variability likely has minimal effects on most species. Therefore, existing NASQAN specific conductance measurements should be adequate for most ecological assessments.

Measures of ecological structure and function amenable to Eulerian water-quality networks

Large rivers represent some of the most spatial and temporally complex ecosystems in existence (Power *et al.*, 1995). Several conceptual attempts have been made to predict changes in biological communities along the size gradient of lotic environments (e.g. Vannote *et al.*, 1980; Junk *et al.*, 1989; Welcomme, 1985).

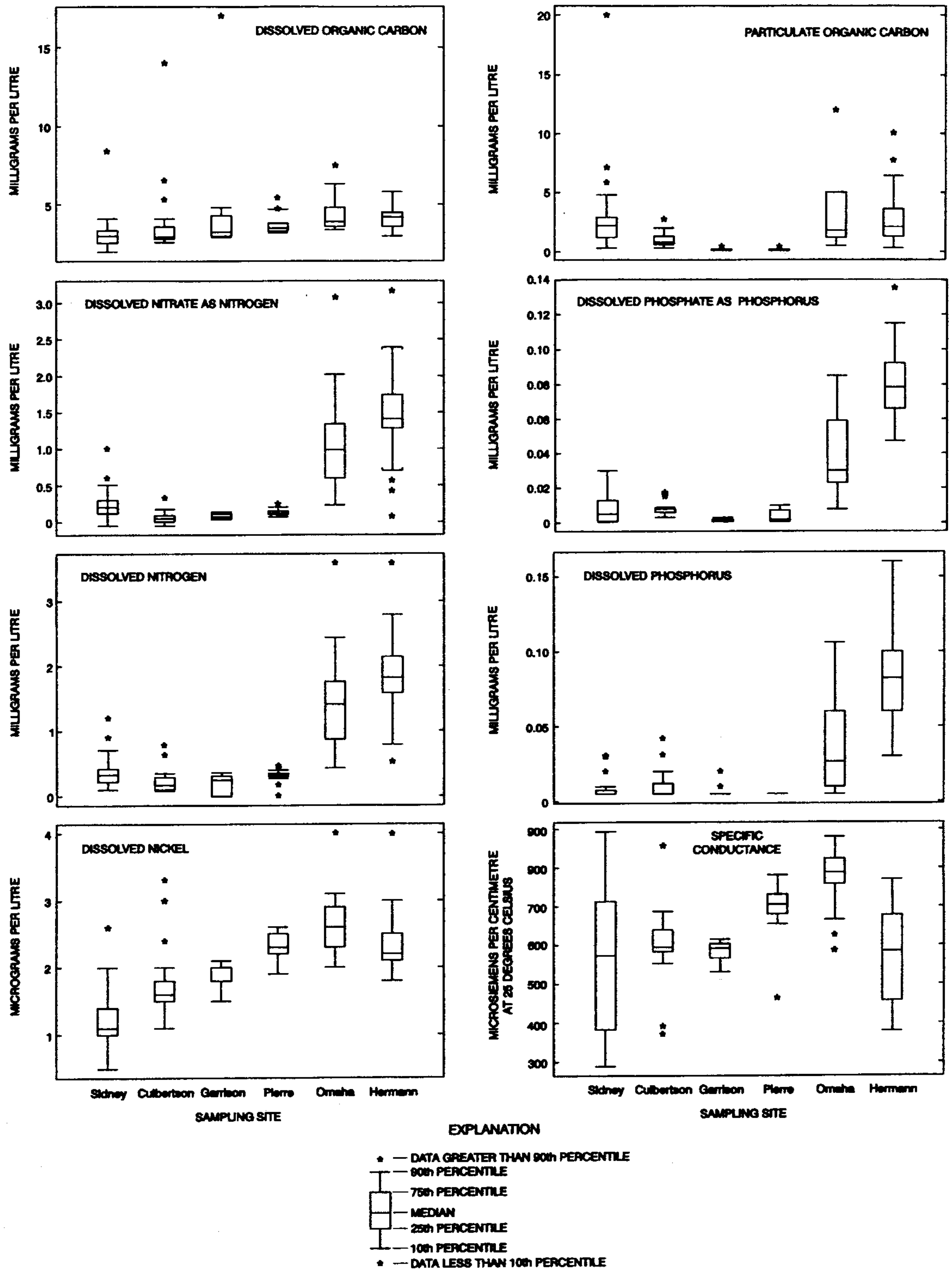

Figure 2. Boxplots of selected NASQAN data in downstream order from the Yellowstone and the Missouri Rivers in 1997 and 1998

However, there is still much that is not known concerning the structure and function of these systems due to the lack of opportunity to study large rivers in their natural state (i.e. most are impounded or channelized) and costs (Power *et al.*, 1995). Theoretical concepts about the effects of reservoirs on numerous limnological characteristics of lotic continuums have been constructed by Ward and Stanford (1983) and are described as the serial discontinuity concept. These conceptual constructs are useful for predicting the character of water quality in the river reaches where no data are available.

Nutrients. Large rivers generally have low primary productivity (Horne and Goldman, 1994) because of high abiotic turbidities that limit light penetration. The larger depths and continual mixing cause phytoplankton to spend most of their time in darkness. Water currents and moving sediments scour attached algae, and fluctuating river stages and shifting sediments can limit the establishment of most macrophytes. Consequently, the food web relies heavily on allochthonous material and the productivity of microbial heterotrophs (Berman, 1988) during decomposition. Allochthonous material received from tributaries often consists of fine refractory organic particles and large tree trunks (Vannote *et al.*, 1980) that have little nutritional value to most organisms. Historically, big rivers received most of their available allochthonous material from the flood plain (Junk *et al.*, 1989) via bank erosion and overbank inundation (Hesse *et al.*, 1988). The historic Missouri River would seem to fit this generalization. However, regulation of flows and stabilization of the channel and flood plain substantially decrease the benefits of these processes. Channel modifications have deepened and narrowed the channel several times from its natural configuration, which would be expected to decrease primary productivity further. Conversely, an increase in water clarity below the reservoirs may increase primary productivity in some reaches (Ward and Stanford, 1983). Levees, replacement of riparian vegetation with agriculture, and stabilization of the river banks have cut off most allochthonous material from the flood plain. Cutting off allochthonous material from the flood plain may decrease both abundance and diversity of fish (Hesse *et al.*, 1988). Therefore, monitoring the energy and nutrient sources to the food web is important to an ecological monitoring program for the Missouri River. Ironically, this loss of inputs may be at least partially offset by inputs of sewage effluents and other anthropogenic sources of carbon, nitrogen, and phosphorus along the Missouri River, though these replacements may not be as available to the food web.

Water-quality parameters that commonly are used to determine or indicate food web characteristics include chlorophyll, dissolved oxygen, dissolved organic carbon (DOC), particulate organic carbon (POC) or volatile suspended solids, turbidity, and various species of nitrogen and phosphorus. In addition, the availability of carbon, nitrogen, and phosphorus to biota is of concern. All these constituents, except chlorophyll, are collected at NASQAN sites. Chlorophyll is a basic indicator of algal populations and primary productivity. Even though primary productivity probably is low in the Missouri River, it is still an important variable in the food web. Therefore, chlorophyll is an important constituent for ecological monitoring on the Missouri River.

Sample analyses that characterize dissolved and suspended carbon are desirable because labile carbon may limit the heterotrophic base of the riverine food web. POC can be expressed as a fraction of the fine particulate (excluding sand) concentration to estimate the carbon content of the sediment. However, the organic content cannot be quantified unless the carbon density of organic material is known. Therefore, selected samples should be analysed for volatile suspended solids or another more direct measure of organic material. Median values of DOC in 1997 and 1998 are similar between, and upstream from, the reservoirs, but DOC increases in the farthest downstream reach (Figure 2) (Kelly and Hooper, 2001) probably reflect an accumulation of refractory carbon. POC is largely removed by the large reservoirs (Figure 2). In addition to DOC and POC, proximate analyses of some samples, to separate organic material into operational fractions based on resistance or susceptibility to sequential extractions and hydrolysis (Preston *et al.*, 1997), or occasional determinations of humic, lignin, tannin, and cutin contents would help to identify changes in the availability or refractory character of organic matter that may result from flood-plain restoration efforts along the lower river. Presumably, allowing the river access to flood plains covered with native vegetation would increase the amount of easily assimilated organic matter.

Colloidal material in three Missouri River samples collected by Rostad and Leenheer (1997) ranged from 4·1 to 6·9% organic carbon, which was similar to silts, but substantially more than the carbon content of sands. The C : N ratios of these colloids were similar to ratios found in algae, fungi, soil-forming bacteria, and microbial cells, and the authors concluded that the primary source of colloidal organic matter was indigenous aquatic microorganisms. Whereas colloidal carbon concentrations would provide valuable information about the nutritional character of suspended sediment, more direct measures of microbial character, such as chlorophyll, adenosine triphosphate (ATP), and organic carbon character are more valuable to most characterizations of biological structure or function. ATP can be used to quantify the biomass of living microbes and thus help characterize the availability of suspended carbon.

Nitrogen and phosphorus often limit primary production in aquatic ecosystems and can cause eutrophication and anoxia in receiving waters such as the Gulf of Mexico (see Goolsby (2001)). Consequently, C : N : P ratios often are used to indicate nutrient availability or limitation. Dissolved nitrogen and phosphorus concentrations increase (Figure 2) (Kelly and Hooper, 2001) and C : N and C : P ratios decrease substantially from upstream to downstream. Although little research has been done on primary producers in the Missouri River, high concentrations of nitrate (Figure 2) indicate that nitrogen is not limiting and, therefore, substantial fixation by cyanophytes is not expected. Although high nitrogen percentages in fine sediments and colloids in the Upper Mississippi River have been attributed to nitrogen-laden sediments from the heavily fertilized farm fields of the Upper Midwest, limited data indicate that the Missouri River may not share this attribute (Leenheer *et al.*, 1995). Concentrations of phosphorus in the upper river usually are less than the detection limit of 0·01 mg l^{-1}. Carbon, nitrogen, and phosphorus increases are especially evident in the dissolved and available inorganic fractions in the lower reach, where both nitrogen and phosphorus are in excess of algal demands. The downstream increases in nitrate and phosphate are evidence that primary production may be light limited rather than nutrient limited in the lower river. Increasing nitrate and phosphorus concentrations also indicate that flood-plain wetlands no longer remove substantial amounts of nitrogen and phosphorus from tributary and flood waters through denitrification and sediment retention. This longitudinal gradient would be better defined with additional stations on the lower river, such as a site just below the lowest reservoir (Yankton, SD), where dissolved nitrogen, phosphorus, and POC would likely be low because of particle settling and primary production in the reservoirs. Addition of this site would allow determination of the full extent of longitudinal changes. However, the small interquartile ranges of nitrogen, carbon, and phosphorus (especially dissolved phases, Figure 2) at most sites indicate that more frequent sampling might not be required for most ecological assessments.

Productivity. Relatively little research has been conducted on primary producers in the lower Missouri ecosystem. However, studies that have examined periphyton communities associated with artificial substrates have indicated that diverse assemblages of diatoms and filamentous algae forms occur with seasonal peaks in late fall (Nelson, 1973; Stern *et al.*, 1974). Primary production in the largely unaltered upper Missouri and Yellowstone Rivers is both allochthonous (i.e. derived from the surrounding terrestrial watershed) and autochthonous (i.e. derived *in situ* from aquatic plants). High water clarity and abundance of stable substrates contribute to significant *in situ* production by periphyton, or the attached periphyton and diatom communities.

Main stem impoundments result in the creation of deep-water lentic habitats where phytoplankton are the dominant source of primary production. Zooplankton are the dominant primary consumers of the algae, which, in turn, support a fish community dominated by zooplanktivores and piscivores.

Primary productivity below the main stem reservoirs is typical of large regulated rivers (Nelson, 1973; Stern *et al.*, 1974; Ward and Stanford, 1983). The aquatic plant communities below the reservoirs are dominated by two major groups of aquatic plants: micro-algae, released from the upstream impoundment, and periphyton, which grows in abundance due to the decreased turbidity of discharged reservoir waters. However, the sources and amounts of primary production change drastically in a downstream direction as the effects of tributaries, light, and over-bank flooding change (Figure 3). Currently, there are no NASQAN parameters that can be used to estimate precisely the levels of *in situ* primary productivity. The addition of chlorophyll analyses would help

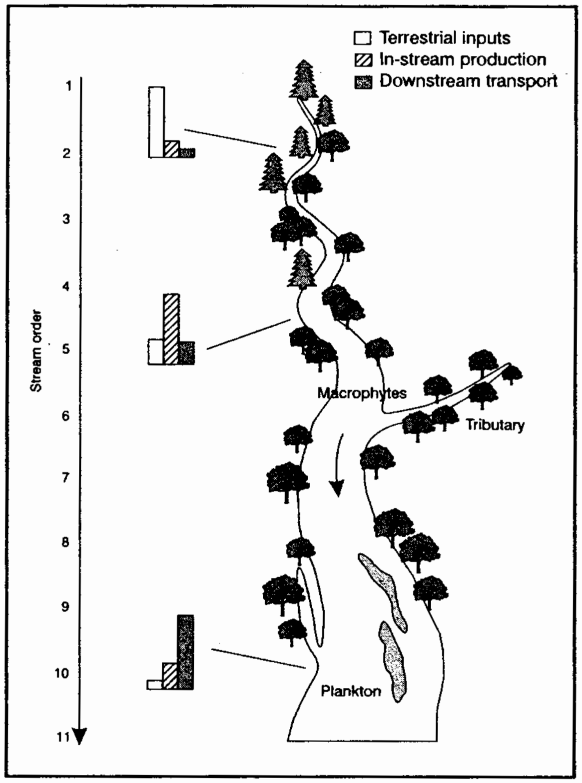

Figure 3. Longitudinal changes in terrestrial inputs, in-stream production, and downstream transport of organic matter typically observed in large rivers; Modified from Vannote, *et al.* (1980) by Johnson (1995). Reproduced by permission of Bioscience and B. Johnson, © 1995 American Institute of Biological Sciences

estimate primary production. However, both suspended and attached forms of algae on surfaces such as rock revetments would have to be assessed to discern seasonal differences in autochthonous *versus* allochthonous sources of carbon. Artificial substrates have been effectively incorporated into Eulerian monitoring programs to evaluate periphyton and would be a valuable addition to NASQAN. Because of low primary productivity in free-flowing reaches, the temporal variability of chlorophyll concentrations will likely be smaller in free-flowing rivers than in reservoirs. Therefore, existing NASQAN sampling frequencies are probably adequate at the free-flowing sites (12 to 15 times per year), but an increase in temporal resolution from six to 12 times per year would improve estimates of sources and patterns of primary productivity at sites just below reservoirs. Characterizations of primary productivity, in relation to total nitrogen and phosphorus, could lead to insight into the trophic functions of the river.

Invertebrates. The invertebrate community of the Missouri River system, much like primary producers, varies spatially due to the changing hydrologic conditions (e.g. increasing streamsize, changing geologic conditions, impoundment). The upper, unchannelized reaches have largely a sand, gravel, and cobble substrate that is hydrologically arranged to result in a diversity of habitats for invertebrates (Dieterman *et al.*, 1996). The invertebrate community of the upper, unchannelized reaches is dominated by benthic macroinvertebrates. Numerous functional feeding guilds, including shredders, scrapers, collectors, filterers, and predators, are present. Though zooplankton are present in standing backwaters and are important food resources for larval fish, hydrologic conditions make the upper reaches a harsh environment for zooplankton.

In contrast, the invertebrate communities of the impounded sections of the Missouri River are dominated by the zooplankton. Lack of current, high-light penetration, and an abundance of phytoplankton result in typical lentic habitats. Macroinvertebrate communities are dominated by filterers and collectors that utilize the small particle sizes of organic matter that are contributed by the phytoplankton community.

Riverine areas downstream of the main stem dams exhibit invertebrate communities typical of regulated rivers. High numbers of zooplankton are merely released into the downstream sections via the discharge of reservoir water (Williams, 1973; Ward and Stanford, 1983). Further downstream, the macroinvertebrate community is dominated by benthic organisms (Poulton *et al.* 1999).

Unfortunately, the spatial variability of bottom sediments and macroinvertebrate distributions is not easily measured by a fixed-site monitoring program, where samples are usually collected from bridges. Benthic invertebrates would probably best be monitored in a separate ecological monitoring program. However, flow mixing of zooplankton makes sampling from bridges at fixed sites possible, and as the flood-plain restorations and the amount of standing backwaters increase, the abundance and composition of zooplankton may change, thereby changing the structure of the food web. Consequently, enumeration of zooplankton by family could be useful for identifying changes in larval fish growth and survival.

Measures of ecotoxicity amenable to Eulerian water-quality networks

Organic analytes. Many of the organic chemicals that are monitored within the NASQAN system are hydrophilic (e.g. atrazine) and are, therefore, easily transported. Many of these chemicals are known or suspected carcinogens that often are not removed during water treatment processes. Thus, NASQAN has provided valuable data concerning the human risks of consuming contaminated drinking water. Monthly sampling probably is adequate to characterize concentrations of hydrophilic herbicides, except during May through July when the majority of herbicides are mobilized and enter the river in the lower reaches (Thurman *et al.*, 1991). Though weekly sampling would be desirable in May through July, use of the three high-water samples (Table I) during the May through July period would substantially improve the characterization of hydrophilic herbicides.

Many organic toxins are hydrophobic and partition into organic colloids (Rostad *et al.*, 1994), fine sediments, plants, and the fatty tissues of animals. Therefore, contaminant loads are highly related to the deposition and transport of sediments, and are most transportable and most available to heterotrophic bioaccumulators. Hydrophobic chemicals such as dioxins, polychlorinated hydrocarbons (PCBs), and organochlorine pesticides exhibit low solubility in water and are not measured in the current NASQAN program. Historically, hydrophobic contaminants were monitored nationwide within the National Contaminant Biomonitoring Program (NCBP) conducted by the U.S. Fish and Wildlife Service from 1967 to 1990 (Schmitt and Bunck, 1995). Residues were monitored in tissues of fish and birds due to suspected effects of these chemicals on bald eagle and other wildlife reproduction. Eventually, this program was expanded to monitor PCBs and other hydrophobic industrial compounds. Many of these insecticides are declining in concentration in the environment because they are no longer used in the USA (e.g. DDT and chlordane); however, these chemicals are used in other countries and are suspected of being transported globally by atmospheric pathways. The former NCBP has been replaced by the U.S. Geological Survey's Bioassessment of Status and Trends (BEST) program. The previous approach to biomonitoring is being reevaluated to determine the complementarity of the BEST fish design with NASQAN and to consider biochemical indicators of contaminants, because many newer generation pesticides (e.g. pyrethroids, organophosphates, and carbamates) and industrial chemicals (e.g. polyaromatic hydrocarbons) do not bioaccumulate in animal tissues.

The measurement of hydrophobic contaminants should be considered within an ecological monitoring program. Newer approaches for assessment of hydrophobic contaminants include the use of semipermeable membrane devices (SPMDs) (McCarthy and Gale 2001; Huckins *et al.*, 1996). SPMDs have the advantage of simulating the uptake of hydrophobic contaminants across membranes but do not exhibit the losses of compounds such as polyaromatic hydrocarbons that typically are metabolized and excreted by organisms such as fish. Further advantages of SPMDs are that they are easier to analyse than tissues and exhibit increased statistical replicability compared with tissue analysis (e.g. they are immobile and are not affected by biological is small in near-neutral surface waters. In fact, more than one-third of the trace elements analysed have concentrations below the minimum reporting level in more than 70% of the NASQAN samples (Kelly and Hooper, 2001). Therefore, when an allochthonous increase in dissolved trace-element concentrations occurs, it is rapidly adsorbed by abundant sediment in the river. Conversely, when an allochthonous dilution occurs, trace elements can be released from the large particulate pool to fill rapidly a much-smaller dissolved pool that tends toward a quasi-equilibrium concentration. This quasi-equilibrium is reflected in the small range of variation of most trace element concentrations found in existing NASQAN data (e.g. nickel in Figure 2, NASQAN data —Mississippi Basin, 1996–1998). Therefore, though biological uptake and decomposition also could cause autochthonous changes in dissolved trace element concentrations, physical autochthonous processes may limit the value of dissolved trace-element concentrations in flux and source investigations. Because total trace element concentrations are not subject to such autochthonous processes, they might be more valuable for flux and source determinations.

The solubilities of major ions are high and the sizes of their dissolved pools are large. Most of them, especially chloride, sodium, and sulfate, are relatively conservative biologically in oxidizing conditions. Even decomposition, which can release dissolved constituents into the water column, adds limited amounts of these constituents, because most highly-soluble material is removed from detritus long before it enters the river. Therefore, autochthonous biological processes are not expected to have large effects on the concentrations of these ions.

Pesticides

Most of the commonly detected NASQAN pesticides (i.e. triazine and acetanilide herbicides and their metabolites) are subject to degradation and are most commonly found in the largest concentrations on the lower river. However, the aquatic degradation rates of these constituents are small compared with the limited amount of travel time available on the lower river (typically 1 week between Omaha and Hermann). Therefore, conservative assumptions are not likely to jeopardize source and transport interpretations.

SUMMARY AND CONCLUSIONS

The enhancement of existing water-quality programs on the Missouri River to address ecological processes has been of interest to many (Missouri River Natural Resources Committee, 1998). Water-quality measures of ecosytem character can be grouped into measures that describe physical habitat, biological structure and function, and ecotoxicity. Although numerous ecological monitoring changes have been recommended, additions that are expected to provide the most information for the least cost are summarized in Table II.

Several items in Table II require hourly measurement, which would add an entirely new operational aspect to the NASQAN program. However, the presence of data loggers and satellite transmitters in the gauging stations at all NASQAN sites substantially improves the feasibility of continuous water-quality monitoring.

In addition to the changes in Table II, the development of relations between discharge, turbidity, and POC would be of benefit in the evaluation of rapid changes in the character of habitat and organic carbon. Collecting samples on free-flowing reaches using a Lagrangian technique, which separates sample collection at different sites by the travel time between sites, would add statistical power to the data when trying to determine differences between sites.

The effects of biological processes, such as decomposition, algal uptake, and denitrification on assumptions of chemical conservatism used in some source and transport interpretations are potentially large for constituents such as organic carbon, organic nitrogen, and dissolved species such as phosphate and inorganic nitrogen in nonwinter months. However, total phosphorus and, probably, nitrogen concentrations are more likely to exhibit conservative behaviour, as most species transformations do not affect total concentrations. Additional studies on decomposition rates in the Missouri River would be of great benefit in evaluating the degree of conservatism exhibited by several chemical species.

Table II. Summary of increases to NASQAN needed to address major ecological processes and issues on the Missouri River

Additional sites and sampling frequency	Increased frequency at all sites or as indicated	Additional constituents at all sites
Yankton, SD (six times/year)	Water temperature (hourly)	Chlorophyll; adenosine triphosphate (ATP)
St. Joseph, MO (15 times/year)	Turbidity (hourly)	Selected lipid-soluble hydrophobic organics such as dioxins, organochlorine pesticides, and polychlorinated biphenols (using SPMDs)
Kansas River at DeSoto, KS (15 times/year)	Dissolved oxygen (hourly during growing season)	Mercury and other trace elements in the total phase with high aquatic toxicities
Waverly, MO (15 times/year)	Chlorophyll (below dams)	Characterization of organics on selected samples (e.g. proximate analyses; humin/lignin contents) and volatile suspended solids on selected samples
Boonville, MO (15 times/year)	Hydrophilic pesticides (weekly in May and June)	Identification and enumeration of zooplankton
		Nonophenol and other potential endocrine disruptors

REFERENCES

Battaglin WA, Kendall C, Chang CCY, Silva SR, Campbell DH. 2001. Chemical and isotopic evidence of nitrogen transformation in the Mississippi River, 1997–98. *Hydrological Processes*. this issue.

Berman T (ed.). 1988. The Role of Microorganisms in Aquatic Ecosystems. *Hydrobiologia* **159**(special issue): 313.

Bowie JE, Petri LR. 1969. Travel of solutes in the lower Missouri River. *US Geological Survey Hydrologic Investigations Atlas HA-332*.

Brumbaugh WG, Petty JD, Huckins JN, Manahon SE. 1999. Development of a passive integrative sampler for labile metals in water. *US Geological Survey Water Resources Investigation Report 99–4018A*, vol. 1; 93–98.

Chapman DC, Allert AL, Fairchild JF, May TW, Schmitt CJ, Callahan EV. 1999. Toxicity and elemental contaminant concentrations of groundwater, sediment pore waters, and surface waters of the Missouri River associated with a metals refining site in Omaha, NE. *US Geological Survey Biological Resources Division Technical Report to the USEPA*, under IAG DW14952122-01-1, Columbia Environmental Research Laboratory, Columbia, MO.

Dieterman DJ, Ruggles MP, Wildhaber ML, Galat DL (eds.). 1996. Population structure and habitat use of benthic fishes along the Missouri and Lower Yellowstone Rivers. *1996 Annual Report to Missouri River Benthic Fish Study PD-95-5832*, to Army Corps of Engineers and US Bureau of Reclamation. Cooperative Fish and Wildlife Research Unit, University of Missouri, Columbia, MO; 270.

Echols KR, Gale RW, Schwartz TR, Huckins JN, Williams LL, Meadows JC, Orazio CE, Petty JD, Tillitt DE. 1999. Evaluation of polychlorinated biphenyl contamination in the Saginaw River using sediments, caged fish and SPMDs. In *U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting*, Charleston, SC, 8–12 March Morganwalp DW, Buxton HT (eds). Vol. 2 Contamination of Hydrologic Systems and Related Ecosystems. *US Geological Survey Water-Resources Investigations Report 99-4018B*; 35–40.

Ford JC. 1982. *Water quality of the lower Missouri River, Gavins Point Dam to mouth*. Missouri Department of Natural Resources, Division of Environmental Quality; 35.

Funk JL, Robinson JW. 1974. *Changes in the channel of the Lower Missouri River and effects on fish and wildlife*. Aquatic Series No. 11. Missouri Department of Conservation: Jefferson City, MO.

Galat DL, Fredrickson LH, Humburg DD, Bataille KJ, Bodie JR, Dorhrenwend J, Gelwicks GT, Havel JE, Helmers DL, Hooker JB, Jones JR, Knowlton MF, Kubisiak J, Mazourek J, McColpin AC, Renken RB, Semlitsch RD. 1998. Flooding to restore connectivity of regulated, large-river wetlands. *Bioscience* **48**: 721–733.

Goolsby DA. 2001. Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA. *Hydrological Processes*: this issue.

Hesse LW, Wolfe CW, Cole NK. 1988. Some aspects of energy flow in the Missouri River ecosystem and a rationale for recovery. In *The Missouri River: the Resources, Their Uses and Values*. Benson NG (ed.). North Central Division, American Fish Society, Special Publication No. 8; 13–29.

Hesse LW, Schlumach JC, Carr JM, Keenlyne KD, Unkenholz DG, Robinson JW, Mestl GE. 1989. Missouri River fishery resources in relation to past, present, and future stresses. *Canadian Special Publication of Fish Aquatic Science* **106**: 352–371.

Holtschlag DJ. 2001. Optimal estimation of suspended-sediment concentrations in streams. *Hydrological Processes*: this issue.

Hooper RP, Aulenbach RP, Kelly VJ. 2001. The National Stream Quality Accounting Network: a flux-based approach to monitoring the water quality of large rivers. *Hydrologic Processes*: this issue.

Horne AJ, Goldman CR. 1994. *Limnology*. 2nd edn. McGraw-Hill Inc.; 576.

Horowitz AJ, Elrick KA, Smith JJ. 2001. Annual suspended sediment and trace element fluxes in the Mississippi, Columbia, Colorado, and Rio Grande drainage basins. *Hydrologic Processes*: this issue.

Huckins JN, Petty JD, Lebo JA, Orazio CE, Prest HF, Tillitt DE, Ellis GS, Johnson BT, Mauweera GK. 1996. Semipermeable membrane devices (SPMDs) for the concentration and assessment of bioavailable organic contaminants in aquatic environments. In Ostrander GK (ed.). Lewis Publishers, Boca Raton, FL; 625–655.

Johnston CA. 1993. Mechanisms of wetland water quality interaction. In *Constructed Wetlands for Water Quality Improvement*, Moshiri GA (ed.). CRC Press: Boca Raton, FL; 293–299.

Johnson BL. 1995. Past, present, and future concepts in large river ecology. *Bioscience* **45**(3): 134–141.

Junk WJ, Bailey PB, Sparks RE. 1989. The flood pulse concept in river-flood-plain systems. In *Proceedings of the International Large River Symposium*, Dodge PD (ed.). Canadian Special Publication on Fishery and Aquatic Science, 106.

Leenheer JA, Barber LB, Rostad CE, Noyes TI. 1995. Data on natural organic substances in dissolved, colloidal, suspended-silt, -clay, and bed-sediment phases in the Mississippi River and some of its tributaries, 1991–92. *US Geological Survey Water Resources Investigations Report 94–4191*; 47.

Kelly VJ, Hooper RP. 2001. NASQAN—The USGS National Stream-Quality Accounting Network: URL http://water.usgs.gov/nasqan Accessed 23 February 2001.

Magnuson JJ, Crowder LB, Medvick PA. 1979. Temperature as an ecological resource. *American Zoologist* **19**: 331–343.

Mathews JJ. 1961. *The Osages*. University of Oklahoma Press: Norman, OK; 829. (Margry P. Decouvertes et etablissements des francais dans l'ouest et dans le sud de l'Amerique Septentrionale. 1614–1754.)

McCarthy KA, Gale RW. 2001. Evaluation of persistent hydrophobic organic compounds in the Columbia River basin using semipermeable-membrane devices. *Hydrological Processes*: this issue.

Missouri River Natural Resources Committee. 1998. Missouri River Environmental Assessment Program US Geological Survey, Columbia, MO; 33.

Moody JA. 1993. Evaluation of the Lagrangian scheme for sampling the Mississippi River during 1987–90. *US Geological Survey Water Resources Investigations Report 93–4042*; 31.

NASQAN Data—Mississippi Basin. 1996–1998. Available from World Wide Web: http://www.water.usgs.gov/public/nasqan/data/final data. Referenced 1999.

Nelson G. 1973. Primary productivity and periphyton standing crops. In *An Ecological Study of the Missouri River Prior to Channelization*, Schlumbach JC (principle investigator). Completion Report Number B-024-SDAK, Water Resources Institute: Brookings, SD; 18–20.

Power ME, Sun A, Parker G, Dietrich WE, Wootton JT. 1995. Hydraulic food-chain models. *Bioscience* **45**: 159–167.

Poulton B, Fairchild JF, Wildhaber M. 1999. Benthic macroinvertebrates associated with specific habitats and substrates of the Lower Missouri River. *Proceedings of the 47th Annual Meeting of the North American Benthological Society*, 15–28 May, Duluth, MN.

Preston CM, Trofymow JA, Sayer BG, Niu J. 1997. ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic-angle spinning investigation of proximate-analysis fractions used to assess litter quality in decomposition studies. *Canadian Journal of Botany* **75**: 1601–1613.

Rostad CE, Leenheer JA. 1997. Organic carbon and nitrogen content associated with colloids and suspended particulates from the Mississippi River and some of its tributaries. *Environmental Science and Technology* **31**(11): 3218–3225.

Rostad CE, Monsterleet SG, Bishop LM, Ellis GS. 1994. Polychlorinated biphenyls associated with suspended silt and clay and colloid from the Mississippi River and some of its tributaries, July 1991 to November 1991. *US Geological Survey Open-File Report 94–484*; 50.

Schmitt CJ, Bunck CM. 1995. Persistent environmental contaminants in fish and wildlife. In *Our Living Resources*. US Geological Survey, 530; 413–416.

Stahlschmidt-Allner P, Allner B, Roembke J, Knacker T. 1997. Endocrine disrupters in the aquatic environment. *Environmental Science and Pollution Research International*, **4**: 155–162.

Stern DH, Wharton SR, Stern MS. 1974. Periphyton and chlorophyll a of the lower Missouri River during 1973. *Presentation to the 22nd Annual Meeting of the Midwest Benthological Society*, 27–29 March, Cincinati, OH.

Thomas P. 1997. Mechanisms of reproductive neuroendocrin toxicity. Crisp Data Base, National Institutes of Health, University of Texas at Austin, Port Aransas, TX.

Thurman EM, Goolsby DA, Meyer MT, Kolpin DW. 1991. Herbicides in surface waters of the Midwestern United States; the effect of spring flush. *Environmental Science and Technology*, **25**: 1794–1796.

US Geological Survey. 1973–1998. Water Resources Data—Missouri. MO Water-Data Reports. Rolla, MO; published annually.

Vannote RL, Minshall GW, Cummins KW, Sedell J, Cushing CE. 1980. The river contimuum concept. *Canadian Journal Fishery and Aquatic Science*, **37**: 130–137.

Ward JV, Stanford JA. 1983. The serial discontinuity concept of lotic ecosystems. In *Dynamics of Lotic Ecosystems*, Fontaine TD, Bartell SM (eds). Ann Arbor Science: Ann Arbor, MI; 29–42.

Welcomme RL. 1985. River fisheries. *FAO Fisheries Technical Paper No. 262*. UN Food and Agriculture Organization: Rome, Italy.

Williams WD. 1973. Zooplankton abundance and distribution. In *An Ecological Study of the Missouri River Prior to Channelization*, Schmulbach JC (principle investigator). Completion Report Number B-024-SDAK, Water Resources Institute: Brookings, SD; 34.